

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : <b>C08G 18/02, 65/48, C08L 23/26, 25/06, 33/08, B27N 3/02, B32B 5/16, D04H 3/16</b>		A1	(11) International Publication Number: <b>WO 98/27131</b> (43) International Publication Date: <b>25 June 1998 (25.06.98)</b>
(21) International Application Number: <b>PCT/US97/22489</b>		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: <b>9 December 1997 (09.12.97)</b>		Published <i>With international search report.</i>	
(30) Priority Data: <b>08/768,617 18 December 1996 (18.12.96) US</b>			
(71) Applicant: <b>PHENIX BIOCOMPOSITES, INC. [US/US]; 1511 North Gault, St. Peter, MN 55113 (US).</b>			
(72) Inventor: <b>RIEBEL, Michael, J.; 100 Deer Place, Mankato, MN 56001 (US).</b>			
(74) Agent: <b>MUETING, Ann, M.; Muetting, Raasch, Gebhardt &amp; Schwappach, P.A., P.O. Box 581415, Minneapolis, MN 55458-1415 (US).</b>			

(54) Title: **FUSED MULTIPARTICLE POLYMERIC MATRIX MATERIAL AND METHOD OF MAKING**

(57) Abstract

A fused multiparticle polymeric matrix material that includes fused discrete thermoplastic particles, wherein the particles have generally distinct boundaries once fused.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**FUSED MULTIPARTICLE POLYMERIC MATRIX MATERIAL**  
**AND METHOD OF MAKING**

**Field of the Invention**

5        The present invention relates to a material made by fusing thermoplastic particles. The resultant material includes particles that have generally distinct boundaries once fused, and thereby emulates the aesthetic characteristics of stone (e.g., granite). Such material can be used for countertops, tiles, flooring, etc.

10

**Background of the Invention**

Currently, there are a number of poured organic polymeric countertop materials made from organic polymerics such as acrylic, polyester, and other blends. These products are commercially available, for examples, under the tradenames CORIAN, AVONITE, and GIBRALTER. Such products are typically 15 made by casting, although they may be extruded in some situations.

Other organic polymeric products are made by injection molding or compression molding organic polymeric pellets, or thermoforming organic polymeric sheets, for example. Typically, such methods cause the organic polymeric particles and sheets to melt and flow, thereby eliminating any discrete 20 particles or boundaries and forming a homogeneous material.

Various attempts have been made to produce solid surface materials (e.g., countertops) with a stone-like (e.g., granite-like) look. One method that has been used is to suspend acrylic chips in a liquid acrylic. This method is not very effective, however, because the resultant material lacks the random fractal geometry 25 of stone such as granite.

The only known synthetic material that has a random fractal geometry is a rigid biocomposite pressure-formed material produced upon fusing discrete fiber-reinforced protein-based biocomposite particulate material under elevated pressure and temperature. This material is available from Phenix 30 Biocomposites, St. Peter, MN. It has a granite-like look and can be engineered to meet the physical characteristics of wood. Although this material could be treated to repel water, there is a need for a more water resistant material that could be used for countertops and other products that contact water.

Summary of the Invention

The present invention provides a structurally rigid organic polymeric pressure-formed material produced from thermoplastic particulate material (i.e., particles) upon fusing the particulate material under elevated pressure and 5 temperature. The individual particles maintain generally distinct boundaries once fused. The particles can be of varying compositions, sizes, shapes, colors, etc. This fusing of particles results in the formation of a pressure-formed material that can exhibit a stone-like granular appearance, e.g., a colorized pattern resembling granite or other natural stones. Thus, the pressure-formed material of the present invention 10 is a fused multiparticle polymeric matrix material. As used herein, "matrix" refers to an array of different particles in a random fractal geometry. The invention also provides a process necessary to fabricate such products, e.g., such as solid surface materials suitable for use as countertops, tiles, and flooring, as well as alternatively shaped pressure-formed materials.

15 The particulate material includes thermoplastic particles that are capable of being fused under elevated temperatures and pressures into a rigid material wherein the fused particles maintain generally distinct and well-defined boundaries. The particulate material can also include thermoset particles that do not necessarily fuse to each other, but can be incorporated within the matrix of the fused 20 thermoplastic particles. Also, the particulate material can include inorganic materials such as particles of metals and minerals, as well as discrete fiber-reinforced protein-based biocomposite particulate material as disclosed in International Publication No. WO 95/04779 (published February 16, 1995), etc. Particularly preferred pressure-formed materials also include a secondary 25 thermosetting binder, such as an isocyanate, preferably an aromatic isocyanate, for enhanced mechanical and physical properties. Such secondary thermosetting binders allow for a variety of dissimilar particulates to be used that would not necessarily effectively fuse together under only the application of heat and pressure.

30 The discrete particles, whether they be just thermoplastic particles or mixtures of thermoplastic particles with other organic polymeric particles (e.g., thermoset particles), inorganic particles, or biocomposite particles, preferably have an average particle size of no greater than about 2 cm. The thermoplastic particles,

whether used alone or in combination with other particles, are capable of forming a rigid organic polymeric material having a Modulus of Rupture of about 1000-4000 pounds per square inch (psi) and a Modulus of Elasticity of about 100,000-400,000 psi (when tested in accordance to ASTM D-1037-91). Typically, with the use of the

5 secondary thermosetting binder (e.g., an aromatic isocyanate), the rigid biocomposite pressure-formed material has a Modulus of Rupture of greater than about 2000 psi, preferably, greater than about 3000 psi, and more preferably, greater than about 3200 psi, and a Modulus of Elasticity of greater than about 100,000 psi, preferably, greater than about 200,000 psi, and more preferably, greater than about

10 300,000 psi.

The present invention is also directed to a method of preparing these fused multiparticle matrix materials. The particles are fused into a rigid pressure-formed material by pressing them under an elevated temperature and pressure. The temperatures used are within a range that allows the particles to soften sufficiently

15 to fuse together, but not to melt and flow. This temperature range is one that causes the particles to become "viscoelastic" (i.e., soften) but not liquid, and is dependent on the type of thermoplastic particulate material. Preferably, a temperature of about 60-300°C is used to cause the thermoplastic particulate material to become viscoelastic. The pressures used are within a range that removes void space

20 between the viscoelastic particles and assists in fusing the particles together. Preferably, a pressure of about 500-2500 psi is used during the formation of the pressure-formed material. In particularly preferred embodiments, the particles used, whether just the thermoplastic particles or the thermoplastic particles in combination with thermoset particles, inorganic particles, or biocomposite particles,

25 are coated (e.g., spray-coated) with a secondary thermosetting binder prior to fusing the particles into a rigid organic polymeric pressure-formed material (i.e., fused multiparticle polymeric matrix material).

Various advantages and distinctions of the present invention will become more apparent from the following detailed description, including the figures

30 and examples.

#### Brief Description of the Drawings

Figure 1 is a photograph of the granular structure and stone-like appearance of a section of the pressure-formed material of the present invention.

5

#### Detailed Description of Preferred Embodiments

The present invention provides a structurally rigid organic polymeric pressure-formed material made from thermoplastic particulate material, optionally in combination with thermoset particles (e.g., urethane or rubber), inorganic particles of metals (e.g., aluminum or brass particles) and minerals (e.g., mica, 10 gypsum, vermiculite, or silica), as well as other particulate material such as discrete fiber-reinforced protein-based biocomposite particulate material as disclosed in International Publication No. WO 95/04779 (published February 16, 1995), which is incorporated herein by reference. The individual particles can also include a colorant if desired. Typically, for the desired appearance, a mixture of a variety of 15 particles of differing colors are used. Furthermore, mixtures of particles having different clarity and translucency can be used. Also, mixtures of particles having different compositions, e.g., types of polymer and fillers, for example, can be used. Once fused into a structurally rigid product, through compression molding, for example, the particles maintain generally well-defined and distinct boundaries 20 forming irregularly shaped domains. Thus, the present invention provides fused multiparticle matrix materials that can have a stone-like granular appearance.

Thus, particles of varying shades and colors can be combined to form products that exhibit colorized patterns resembling granite and other natural stones of an igneous nature. That is, a granular appearance can be exhibited which in one 25 instance closely resembles granite. Other appearances are attainable upon varying the concentrations of the sized particulates and colorants, however. Figure 1 is a photograph of the granular structure and stone-like appearance of a section of pressure-formed material of the present invention.

Such pressure-formed materials of the present invention are generally 30 impervious to water, and generally resistant to impact and abrasion under normal conditions of use (e.g., when used as a kitchen or bathroom countertop). The density and machinability characteristics of the rigid pressure-formed materials are

similar to solid surface materials currently on the market for use in countertops, for example.

Thus, the present invention provides irregularly patterned, multi-colored (e.g., granite-like) rigid organic polymeric pressure-formed materials. Such 5 granite-like patterns have never before been accomplished in organic polymeric materials. Thus, the materials of the present invention result from an appreciation of the process of forming natural stone and the relationship of human perceptions of natural stone. That is, natural stone is formed from densely packed random crystals of variously colored minerals, which, over time in response to specific 10 physical laws, combine and tend toward a minimum energy system. Such a process parallels recent understandings of the theories of ordered chaotic systems. Human eye-brain perceptions, in contrast, are learned. Thus, any recognition and appreciation that a material is "natural" or "artificial" is formed upon a mental comparison to learned perceptions. Because the artificially produced materials of 15 the invention closely approximate the natural random crystal ordering of igneous stone, particularly granite, the resultant material is perceived to be stone.

The thermoplastic particles are typically in the form of generally hard irregularly shaped lumps or balls. Preferably, they are in the form of conchoidal fractured particles (i.e., a fractured form typically occurring in minerals as a result 20 of a blow or a process such as hammer milling or granulated). They typically have an average particle size (as determined by the largest dimension of the particle) of no greater than about 2 cm, and often no greater than about 1 cm. Typically, particles larger than this do not generally process well, e.g., press well. The minimum particle size can vary as desired. These particle sizes also apply to the 25 optional thermoset particles, inorganic particles, biocomposite particles, etc.

The thermoplastic particles are capable of being bonded or fused together under heat and pressure, preferably in the presence of a secondary thermosetting binder. This is because the viscoelasticity of the thermoplastic particles can be altered with elevated temperatures and pressures such that the 30 particles are plasticized and softened, but are not flowable. For example, polyester is in a solid state at room temperature and is very strong and highly resistant to reshaping by the application of pressure. At temperatures over 265 °C, polyester

melts and becomes flowable, which is required for injection molding and other forming processes currently being used. There is a range of temperatures, however, within which polyester particles soften and do not flow. This range, which is typically about 60-265°C for polyester, is the "viscoelastic" range wherein the 5 particles maintain their individuality and can be easily reshaped. In this state, pressures of at least about 500 psi can be used to fuse the particles into a pressure-formed article.

As previously stated, it is preferred to include a secondary thermosetting binder. It is believed that a secondary thermosetting binder further 10 cures such that there are resin-resin interactions between the particles, although not to such an extent that the particles flow together and lose their distinct boundaries.

The thermoplastic particles can be formed from organic polymeric materials such as polycarbonate, polyethylene, polystyrene, acrylic, polyester, or other desired organic polymeric materials. Colorants (e.g., pigments or dyes) can 15 be incorporated into the particles or used separately in combination with colorless particles to provide variations in the depth of field in the end product. The particles can be purchased or they can be extruded and optionally hammer milled into the desired shapes and sizes. Minerals, thermoplastic fillers, and fiber fillers, for example, can also be incorporated into the particles to vary the clarity and optical 20 properties of individual particles.

Preferably, the colorant can withstand the processing conditions used herein, e.g., temperatures as high as 200°C. That is, the colorant must be able to maintain color fastness under heat and pressure. Furthermore, the colorant should be UV-stable. Also, each colored particulate material must not significantly bleed 25 or transfer color to adjacent colored particulate material during processing into the pressure-formed products. These requirements are generally met by commercially available inorganic or organic colorants, i.e., dyes or pigments.

Suitable inorganic colorants are generally metal-based coloring materials, such as ground metal oxide colorants of the type commonly used to color 30 cement and grout. Such inorganic colorants include, but are not limited to: metal oxides such as red iron oxide (primarily  $Fe_2O_3$ ), yellow iron oxide ( $Fe_2O_3 \cdot H_2O$ ), titanium dioxide ( $TiO_2$ ), yellow iron oxide/titanium dioxide mixture, nickel oxide,

manganese dioxide ( $MnO_2$ ), and chromium (III) oxide ( $Cr_2O_3$ ); mixed metal rutile or spinel pigments such as nickel antimony titanium rutile ( $\{Ti,Ni,Sb\}O_2$ ), cobalt aluminate spinel ( $CoAl_2O_4$ ), zinc iron chromite spinel, manganese antimony titanium rutile, iron titanium spinel, chrome antimony titanium rutile, copper 5 chromite spinel, chrome iron nickel spinel, and manganese ferrite spinel; lead chromate; cobalt phosphate ( $Co_3(PO_4)_2$ ); cobalt lithium phosphate ( $CoLiPO_4$ ); manganese ammonium pyrophosphate; cobalt magnesium borate; and sodium alumino sulfosilicate ( $Na_6Al_6Si_6O_{24}S_4$ ). Suitable organic colorants include, but are not limited to: carbon black such as lampblack pigment dispersion; xanthene dyes; 10 phthalocyanine dyes such as copper phthalocyanine and polychloro copper phthalocyanine; quinacridone pigments including chlorinated quinacridone pigments; dioxazine pigments; anthroquinone dyes; azo dyes such as azo naphthalenedisulfonic acid dyes; copper azo dyes; pyrrolopyrrol pigments; and isoindolinone pigments. Such dyes and pigments are commercially available from 15 Mineral Pigments Corp. (Beltsville, MD), Shephard Color Co. (Cincinnati, OH), Tamms Industries Co. (Itasca, IL), Huls America Inc. (Piscataway, NJ), Ferro Corp. (Cleveland, OH), Engelhard Corp. (Iselin, NJ), BASF Corp. (Parsippany, NJ), Ciba-Geigy Corp. (Newport, DE), and DuPont Chemicals (Wilmington, DE).

The colorant is typically added to the particulate material without 20 further processing and in an amount suitable to provide the desired color. Preferably, the colorant is present in the particulate material in an amount of no greater than about 15% by weight of the particles, more preferably, no greater than about 10%, and most preferably, no greater than about 3%. The colorant can be in the thermoplastic particles, the optional thermoset particles, or the optional 25 biocomposite particles, for example.

For particularly advantageous results the particulate material is preferably coated with a secondary thermosetting binder, such as an isocyanate, epoxy, phenolic, melamine, or urea-containing binder. Preferably, the secondary thermosetting binder is an organic isocyanate, and more preferably an aromatic 30 isocyanate. The secondary thermosetting binder provides greater mechanical properties, e.g., stiffness and strength, to the pressure-formed products. For example, it decreases the amount of cupping and warping of the pressure-formed

material. The use of secondary thermosetting binder can increase the modulus of elasticity by about 30% or more, and the modulus of rupture by about 50% or more. The thermosetting binder is particularly advantageous when the thermoplastic particulate material is used in combination with thermoset particulate material, 5 inorganic particulate material, and/or biocomposite particulate material.

Suitable isocyanates include, but are not limited to, the aromatic isocyanates 4,4-diphenylmethane diisocyanate (MDI), toluene isocyanate (TDI), xylene diisocyanate (XDI), and methaxylene diisocyanate (MXDI). Preferably, the aromatic isocyanate is MDI. The secondary thermosetting binder can be used in an 10 amount of about 0.5-30%, preferably about 2-10%, based on the total weight of the organic polymeric particles. Preferably, the secondary thermosetting binder is used in an amount of about 3-6%, based on the organic polymeric particles. Advantageously, no hardeners or buffers are required to be used with the aromatic isocyanate, thereby reducing any potential for incompatibility with other additives 15 used in the compositions of the present invention.

The mechanical and physical properties of the pressure-formed materials of the present invention can be readily controlled and engineered as desired. That is, depending on the additives, type of particles, the applied pressure, and the heating schedule, for example, the density, surface hardness, bending 20 modulus, and tensile and compressive strength of the pressure-formed products can be varied.

Depending on the various components, amounts, and processing parameters chosen, values for Modulus of Rupture ("MOR") can range from about 1000 psi to about 4000 psi, and values for Modulus of Elasticity ("MOE") can range 25 from about 100,000 psi to about 400,000 psi (when tested in accordance to ASTM D-1037-91). Typically, with the use of the secondary thermosetting binder (e.g., an aromatic isocyanate), the rigid biocomposite pressure-formed material has a Modulus of Rupture of greater than about 2000 psi, preferably, greater than about 3000 psi, and more preferably, greater than about 3200 psi, and a Modulus of 30 Elasticity of greater than about 100,000 psi, preferably, greater than about 200,000 psi, and more preferably, greater than about 300,000 psi. Typically, the preferred

higher MOR and MOE values can be obtained through the use of high secondary thermosetting resin levels and/or high pressures.

Hardness values will also typically increase with the use of a secondary thermosetting resin. Such increases can range from about 2% to about 5 10%. The hardness, however, typically also depends on the type(s) of particulate material and processing conditions.

In general, the pressure-formed products of the present invention are made by a process that involves fusing the thermoplastic particulate material (optionally with thermoset particulate material, inorganic particulate material, 10 biocomposite particulate material, etc.) described above into a rigid material. Preferably, the process involves obtaining the particles in the desired size and shape and fusing the particles, optionally coated with a secondary thermosetting binder. The particles are typically fused when thermally pressed at a temperature of about 15 60-300°C and a pressure of about 500-2500 psi, for about 1-60 minutes. The resulting material (e.g., shaped object) is suitable for further forming and finishing steps. The raw stock is then finished with appropriate shaping and surface finishing steps, if desired, to produce a final finished product. If used as a laminate or molding accent, a material would typically undergo further preparation for attachment to furniture or possibly ceiling or wall panels.

20 The particulate material can be purchased and used as is or it can be preprocessed if necessary. Such preprocessing can involve melting and reforming the material into particles and/or selecting, sizing, grading, sorting, and storing in appropriate bins in a form ready for subsequent processing. Typically, the thermoplastic particles are purchased in a form ready for use. Preferred 25 thermoplastic particles are referred to as "regrind" and can be purchased in a variety of colors from a variety of commercial sources. Regrind typically comes in a mixture of a broad range of particle sizes.

Once prepared, each of the separate batches of particles, which are typically colorized, can be stored for an unlimited amount of time until combined. 30 The separate colorized batches are combined or admixed in various prescribed proportions to provide a desired particulate material mixture that will yield a reproducible "chaotic" color pattern in the finished product. Typically, at least four

different batches of particles, which can vary by color, clarity, particle shape, particle size, type of particle, type and amount of filler, etc., are used to simulate granite. For example, to provide a product that virtually duplicates the appearance of natural "red granite," the following particles are combined: red polyester (Red PET) particles having an average particle size of about 0.05 cm and 50% translucency with a melt temperature of about 120°C; black modified polyester (Black PET) particles having an average particle size of about 0.9 cm and 100% opacity with a melt temperature of about 120°C; white polyester (White PETG) particles having an average particle size of about 1.2 cm and a milky white appearance with a melt temperature of about 200°C; and red polyester (Red PETG) particles having an average particle size of about 1.2 cm and a milky red appearance with a melt temperature of about 200°C. All of these particles are available from Spartek, Mankato, MN. Interestingly, such PET and PETG particles are typically not compatible in extrusion or compression molding processes, but are compatible in the methods used to make the articles of the present invention.

Alternatively, red granite appearing fused multiparticle matrix material can be prepared by replacing the Red PETG with a red fiber-reinforced protein-based biocomposite particulate material as disclosed in International Publication No. WO 95/04779 (published February 16, 1995). Such biocomposite particulate material includes primarily renewable natural resources, i.e., cellulosic material, such as recycled newspaper, and a protein-based resin prepared from ground leguminous material, such as soy flour. That is, the particulate material is primarily a cellulose-reinforced vegetable protein-based thermosetting resin system. This protein-based resin (also referred to as a legume-based resin) forms the matrix, i.e., the primary binding agent, of the biocomposite particulate material. Preferably, on a dry weight basis, the ratio of cellulose to resin solids, e.g., paper to soy flour, is about 0.8:1.0 to about 1.5:1.0, and more preferably about 1.0:1.0 to about 1.3:1.0. Thus, the amount of the thermosetting resin solids relative to the total amount of resin solids and cellulose solids in the biocomposite particulate material prior to pressure-forming is preferably about 40-56%, and more preferably about 43-50%. The method of making such fiber-reinforced protein-based biocomposite particulate

material is disclosed in International Publication No. WO 95/04779 (published February 16, 1995), which is incorporated herein by reference.

When thermoplastic particles are combined with thermoset particles, inorganic particles, biocomposite particles, etc., to form fused multiparticle matrix 5 material, the thermoplastic particles are preferably used in an amount of at least about 50% by weight, based on the total weight of all the particles prior to coating or fusing. More preferably, the thermoplastic particles are used in an amount of at least about 60% by weight, based on the total weight of all the particles prior to coating or fusing. Most preferably, the thermoplastic particles are used in an 10 amount of at least about 80% by weight, based on the total weight of all the particles prior to coating or fusing.

Mixing of the batches of particulate material of varying types of particles, varying colors of particles, varying degrees of translucency of the particles, etc., can be carried out in a ribbon blender, a screw mixer, a tumble mixer, 15 or any other means typically used in blending particulate material streams (e.g., free-flowing solids). Preferably, a ribbon blender is used to form a generally uniform distribution of the different particles. It is significant to note that there is not discernible color transfer from one particle to another during this blending process. This is at least because stable colorants are chosen such that they do not 20 significantly bleed under these blending conditions or the subsequent processing conditions. Typically, this blending process does not significantly alter the particle size of the particulate material; however, the mechanical mixing process can reduce the size of large particles and break up aggregates of particles. This homogenized mixture is then typically screened to remove any remaining large clumps or 25 aggregates of material that may have formed in the mixing and blending processes. These clumps can be broken apart into smaller particles or discarded as deemed appropriate. Preferably, a screening device having a mesh size of 2 cm or smaller is used. Typically, a vibrating angled diamond screen having a 0.95 cm screen size is used.

30 The pressure-formed material can be produced by a variety of methods. In one method, it is produced by heating and pressing the particulate material at an elevated pressure and temperature in a hot press. As used herein,

"elevated" refers to temperatures and pressures above ambient conditions, i.e., room temperature and atmospheric pressure. The press may be either closed or open as in a caul or screen system, and the material may be pressed to stops or thickness, or pressure. If an open system is used, cold pre-pressing may be necessary for 5 handling purposes. Alternatively, the particulate material can be roll pressed. Preferably, the material is compacted and heated in a one-step pressing operation to compress and optionally further cure the particulate material.

Prior to compressing the particulate material, it is preferably and advantageously coated with a secondary thermosetting binder (e.g., an aromatic 10 isocyanate), and other optional additives, such as a sizing agent for additional water repellency. This can be accomplished by blending the particles with the secondary thermosetting binder and/or other additives using a blender, such as a continuous or batch-type ribbon blender or a batch-type or continuous drum blender, and coating, preferably spray coating using high pressure pumps, air atomizers, 15 mechanical atomizers (e.g., a spinning disc atomizer), or a combination thereof. The secondary thermosetting binder may interact with the particles in the drying step of the process. This can create a dual resin system, e.g., the resin of the particles and an isocyanate resin, which is believed to provide greater advantage than either used alone.

20 The pressures and temperatures used to fuse the particles together are chosen such that the particles do not completely melt and flow, but only soften and are capable of being fused together without losing their discrete boundaries upon compaction. Although the pressure can be applied in a progressive manner, typically it is more efficient to simply apply a constant pressure for a specific period 25 of time. For heated platen systems, the platen temperature during the pressure phase is preferably about 60-300°C, while the pressure is preferably about 500-2500 psi. It is to be appreciated that the compacted particulate material can either be alternately heated and compressed or simultaneously heated and compressed.

30 The duration of the applied heat and pressure are selected in relation to the thickness and desired density of the product being prepared. For example, for a nominal sheet of 1 inch thickness of material containing 80% polyester and 20% fiber-reinforced protein-based biocomposite particulate material as disclosed in

International Publication No. WO 95/04779 (published February 16, 1995), using an electrically heated thermal platen press, an exposure time of about 15 minutes at 750 psi and 116°C produces a suitable sheet. A thermally heated platen press is particularly advantageous at least because it is economical.

5        Depending upon the pressure-formed product being prepared, a suitable heated press is selected that is capable of compacting the particulate material to the desired size and providing a preferred throughput rate and energy consumption. For example, a standard plastic compression molding press, such as that available from Dake Corp., Grand Haven, MI, or PHI Inc., City of Industry, CA,  
10      can be used. Such heated molding presses are suitable for hot pressing a single sheet of fused multiparticle matrix material of the present invention.

In post-conditioning, the sheets can be surface-planed immediately after pressing while they are still hot. The planed sheets are typically stacked, i.e., piled one on top of another, while still hot and covered with an insulating counter  
15      weight flat panel material. The sheets are stored in this fashion for at least about one week prior to sizing and finishing.

At the finishing stage, the pressure-formed product is surface finished, sized, and final shaped according to various market requirements by sanding, planing, sawing, shaping or other appropriate machining. By bonding  
20      individual sheets together, complex shapes and assemblies can be formed. Matrix materials with other materials can also be obtained, such as by inlay. Seamed assemblies preferably are formed from sheets prepared from common color batches to minimize any color differentiation.

A desirable attribute of the sheets produced by either of the processes  
25      is that the material is relatively dense and thus can be finished to form relatively smooth edges and surfaces. Correspondingly, the edges accommodate conventional finger, or butt jointing and other jointing techniques to enable the production of larger, complex pieces from multiple smaller pieces. Also, because of the unique homogeneous color patterns exhibited throughout an entire volume of the produced  
30      product, essentially seamless joints are obtained. Complex shapes, such as corner molding, contours and orthogonal jointed corners can also be formed with invisible seams at the juncture of two pieces of the same material.

A further attribute of derived sheet material is that compositional or inlaid sheets can be fabricated, using the batch processing method. In such instances, separately prepared inlay members, such as commemorative plates, name tags or the like, and which can comprise almost any organic material (e.g., wood or 5 organic polymerics), or inorganic material (e.g., metal) can be inserted into the press mold prior to the pressing step. Once the particles are added and compressed during the molding process, the particulate material forms around and in intimate contact with the inlay material. Upon final curing, a strong contact and bond is made between the inlay and sheet, and the inlay becomes an integral part of the resulting 10 sheet.

Still another attribute of the invention using the process and equipment described above is the ability to machine the upper and/or lower plates either in cameo or intaglio with a desired figure or shape. When the particulate material is pressed in the mold, the sheet material will retain an image of the pattern 15 provided in the mold plate either intaglio or cameo, depending upon whether the mold plate pattern is raised or inset. Upon cooling the sheet, the pattern is retained in fine detail.

The following examples are offered to further illustrate the various specific and preferred embodiments and techniques. It should be understood, 20 however, that many variations and modifications may be made while remaining within the spirit and scope of the present invention. As used in the examples, and elsewhere herein, percentages are weight percentages unless otherwise indicated.

#### Experimental Example

25 A fused multiparticle polymeric matrix material of the present invention was prepared as follows. Materials were purchased from Spartec, a plastic extrusion company located in Mankato, MN. Three types of polyester particulate materials were purchased, referred to as "PET" (natural and opaque white) and "PETG" (clear). The particulate material had a distribution of sizes less 30 than about 1.2 cm. A mixture of 25:25:50 PET (natural) to PET (white) to PETG (clear) was prepared by blending until uniformly distributed. "RUBINATE" MDI form ICI, Inc. was sprayed onto the particles in an amount of about 5% by weight.

Mixing was continued to evenly distribute the MDI. The mixture was placed into a laboratory size mold (23 cm x 9 cm). The mold was electrically heated and was made out of aluminum for improved heat transfer. The temperature and the pressure of the mold were set at 210°C and 750 psi, and the material was

5 compressed until no additional compression was measurable, which was typically about 7-10 minutes. The compressed material was removed from the mold, allowed to cool while on edge to prevent sagging. Once cooled the material was sanded sequentially using 120 and 240 grit sand paper on a "TIMESAVER" sanding machine (Timesaver Corp., Minneapolis, MN). This procedure was repeated except

10 that no MDI was added. The MOR and MOE values were determined according to ASTM D-1037-91. With MDI, the MOR was 3389 psi and the MOE was 368,003 psi. Without MDI, the MOR was 1393 psi and the MOE was 262,319 psi.

Although the invention has been described with respect to various

15 presently preferred mixtures and production equipment, it is to be appreciated that still other methods and mixtures may be suggested to those skilled in the art. Accordingly, it is contemplated that the foregoing description should be interpreted to include all those equivalent embodiments within the spirit and scope thereof.

**WHAT IS CLAIMED IS:**

1. A fused multiparticle polymeric matrix material comprising fused discrete thermoplastic particles, wherein the particles have generally distinct boundaries once fused.
2. The matrix material of claim 1 wherein the thermoplastic particles comprise a mixture of different types of thermoplastic particles.
3. The matrix material of claim 1 which has a stone-like granular appearance.
4. The matrix material of claim 1 having a Modulus of Rupture of about 1000-4000 psi and a Modulus of Elasticity of about 100,000-400,000 psi.
5. The matrix material of claim 1 further comprising a secondary thermosetting binder.
6. The matrix material of claim 5 wherein the secondary thermosetting binder is selected from the group of an isocyanate, epoxy, phenolic, melamine, and urea-containing binder.
7. The matrix material of claim 6 wherein the secondary thermosetting binder comprises an aromatic isocyanate.
8. The matrix material of claim 5 having a Modulus of Rupture of greater than about 2000 psi and a Modulus of Elasticity of greater than about 100,000 psi.
9. The matrix material of claim 5 further comprising fused discrete thermoset particles.
10. The matrix material of claim 5 further comprising fused inorganic particles.

11. The matrix material of claim 5 further comprising fused discrete fiber-reinforced protein-based biocomposite particles.
12. The matrix material of claim 1 which forms a solid surface material.
13. The matrix material of claim 1 wherein the thermoplastic particles comprise a mixture of differently colored particles having different levels of translucency.
14. The matrix material of claim 1 wherein at least about 50% by weight of the particles are thermoplastic particles.
15. A method of preparing a fused multiparticle polymeric matrix material, the method comprising:
  - heating particulate material comprising thermoplastic particles to a temperature effective to cause the thermoplastic particles to become viscoelastic; and
  - pressing the viscoelastic particles under sufficient pressure for a time effective to fuse the particles into a fused multiparticle polymeric matrix material comprising particles having generally discrete boundaries once fused.
16. The method of claim 15 wherein the heating and pressing steps occur simultaneously.

17. The method of claim 15 wherein the particulate material comprises a mixture of different types of thermoplastic particles.
18. The method of claim 17 wherein the particulate material comprises a mixture of differently colored particles having varying degrees of translucency.
19. The method of claim 15 wherein the particulate material is coated with a secondary thermosetting binder prior to being subjected to the heating and pressing steps.
20. The method of claim 19 wherein the particulate material further comprises thermoset particles, inorganic particles, fiber-reinforced protein-based biocomposite particles, or combinations thereof.

1 / 1

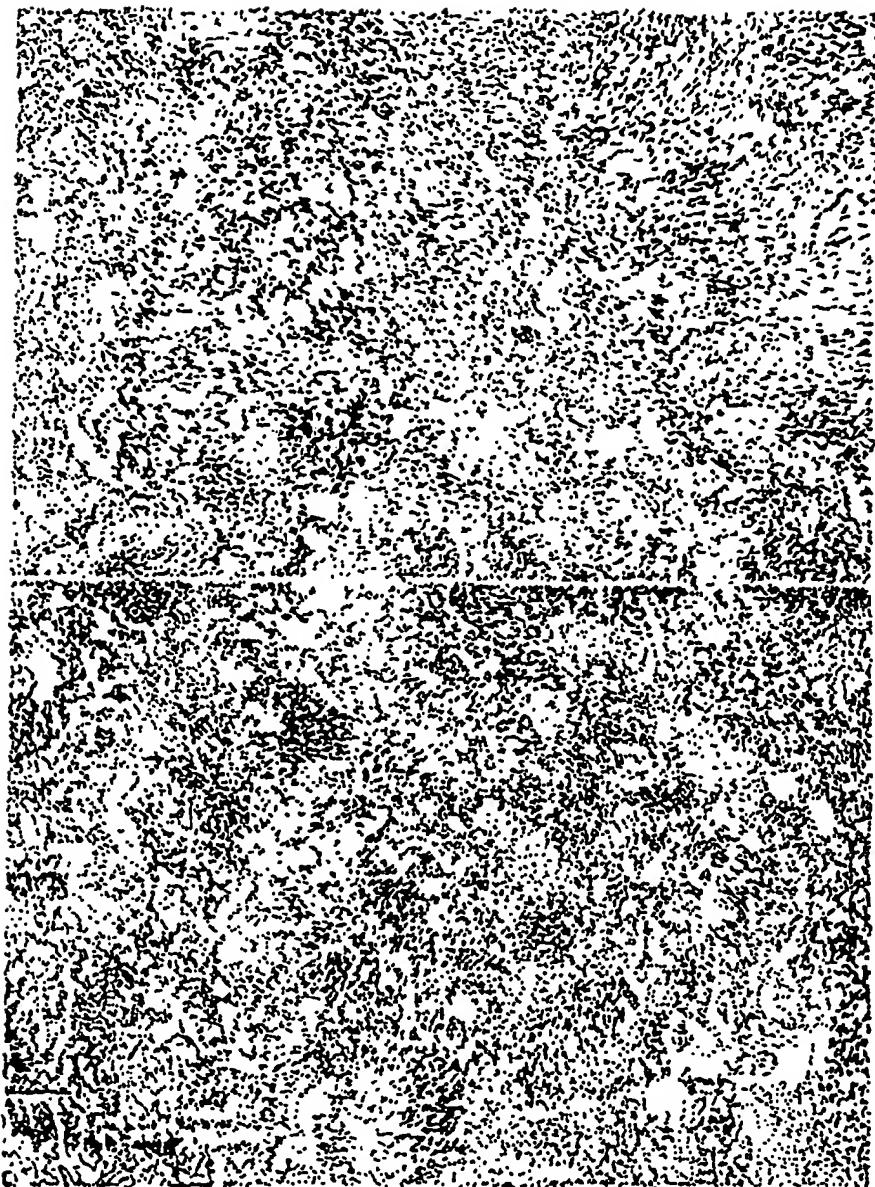


Fig. 1

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/22489

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/221, 222, 240, 241, 390, 391, 392, 404, 408, 418, 452; 264/115, 109, 126; 156/622; 428/326

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: fused particles, discrete, thermolastic

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,923,657 A (GEMBINSKI et al) 08 May 1990, see entire document.	1-4, 12-16
X	US 5,508,095 A (ALLUM et al) 16 April 1996, see entire document.	1-4, 12-16
A,P	US 5,593,625 A (RIEBEL et al) 14 January 1997, see entire document.	1-16

<input type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input type="checkbox"/>	See patent family annex.
"A"	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"B"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"P"	document referring to an oral disclosure, use, exhibition or other means		
	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
03 MARCH 1998	17 MAR 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer <i>B. Shuler</i> MARGARET GLASS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/22489

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

C08G 18/02, 65/48; C08L 23/26, 25/06, 33/08; B27N 3/02; B32B 5/16; D04H 3/16

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

525/221, 222, 240, 241, 390, 391, 392, 404, 408, 418, 452; 264/115, 109, 126; 156/622; 428/326